LINEAR POLYMERS FROM DIOLEFINS AND DIMERCAPTANS

BY

ROBERT ROOD CHAMBERS

A.B., University of Nebraska, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE
UNIVERSITY OF ILLINOIS. 1947

URBANA, ILLINOIS

1947

LINEAR POLYMERS FROM DIOLEFINS AND DIMERCAPTANS

BY

ROBERT ROOD CHAMBERS

A.B., University of Nebraska, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE
UNIVERSITY OF ILLINOIS, 1947

URBANA, ILLINOIS

1947

ACKNOWLEDGMENT

The author would like to express his sincere appreciation to Professor C. S. Marvel for suggesting this study and for his advice during the course of this investigation.

The author is indebted to Professor H. A. Laitinen, Mrs. G. W. Leubner, and Mrs. H. E. Fritz for several amperometric titrations. He would also like to thank Dr. F. A. Miller and Mrs. J. L. Johnson for the infra-red measurements, their graphs and interpretation. The author is grateful to Professor G. L. Clark and Mr. D. L. Leussing for the X-ray diffraction measurements and their interpretation, and for the calculation of the bond distances.

The author is indebted to the Allied Dye and Chemical Corporation and the Monsanto Chemical Company for fellowships.

LINEAR POLYMERS FROM DIOLEFINS AND DIMERCAPTANS

Introduction

It has been shown by several workers that mercaptans add to olefins and that the non-Markownikoff addition proceeds very rapidly and in good yields. Vaughan and Rust using hydrogen sulfide and diolefins, Coffman using dithiols and diolefins and Braun using unsaturated mercaptans have made liquid polymers of low molecular weight by this reaction. A study was made of the use of this reaction to form polymers and of the structure and reactions of the sulfide polymers so formed.

Discussion

Addition of benzyl and butyl mercaptans to several olefins was accomplished in the presence of ultraviolet light and benzoyl peroxide. To demonstrate that non-Markownikoff addition had occurred, the sulfides formed from benzyl mercaptan and styrene, and butyl mercaptan and dodecene-1 were independently synthesized from the mercaptans and the corresponding bromides. Comparison of the sulfones from each pair of sulfides by mixed melting points showed their identity. The addition of butyl mercaptan to styrene was carried out under several conditions, and the yield was calculated from amperometric determinations of the unreacted mercaptan. It was found that benzoyl peroxide, additional oxygen or purified mercaptan did not affect the yield, but that ultraviolet light was very helpful.

Hexamethylenedithiol and biallyl polymerized under the influence of ultraviolet light to form a solid white polymer of molecular weight between 1,000 and 40,000 which was soluble in benzene and chloroform. Model polymers corresponding to Markownikoff and non-Markownikoff addition

of the hexamethylenedithiol to the biallyl were synthesized from hexamethylenedithiol with 2,5-dibromohexane and hexamethylene dibromide respectively. Comparison of the infra-red spectra of the three sulfide polymers indicated the identity of the addition polymer to the solid non-Markownikoff model polymer, and the absence of methyl groups in either polymer. The liquid Markownikoff model polymer had a distinctly different infra-red spectrum in which was indication of the presence of methyl groups.

Among the eighteen structurally different examples of the sulfide polymers which were made by the addition reaction, those which were symmetrical and unbranched were solids, while the branched ones, in general, were liquids. The solid sulfide polymers melted completely over temperature ranges of 1° to 6° at temperatures of 60° to 110° depending on the structure. Inclusion of benzene nuclei, attached in the para position, in the chain, tended to increase the melting point. An increase in melting point was found in the case of hexamethylenedithiol, biallyl polymers of increasing molecular weight.

The X-ray diffraction patterns of the sulfide polymers from ethanedithiol and biallyl, hexamethylenedithiol and biallyl, and decamethylenedithiol and 1,10-undecadiene showed bands very similar to those of crystalline tetracosane. In addition, bands corresponding to the distances between the sulfide groups were found in the patterns. Good agreement between values calculated for these distances and those obtained from the patterns offered further evidence of the unbranched structure of these sulfide polymers.

There were made for use as intermediates, 2-methyl-1,3-propanedithiol and 2,5-hexanedithiol from the corresponding dihalides. Addition of thioacetic acid to diolefins and hydrolysis of these thioesters was used for the preparation of 2-methyl-1,4-butanedithiol and bis(p-β-mercaptoethylphenyl)methane.

Oxidation of certain sulfide polymer samples by small amounts of perbenzoic acid or iodine increased the molecular weight of the sulfide polymers, which indicated that these polymers had thiol end-groups. Oxidation of the sulfide groups in the hexamethylenedithiol, biallyl polymer could be accomplished by perbenzoic acid or potassium permanganate to form a very insoluble polysulfone melting at 194°.

Undecylenic mercaptan, obtained by hydrolysis of the isothiouronium salt, polymerized quickly to form a solid, white polymer. Attempts to form polymers from acetylenic compounds were unsuccessful in the case of acetylene, but ethylacetylene formed a small amount of polymer which, analysis indicated, consisted about half of units obtained by addition of two sulfhydryl groups to the triple bond, and about half of disulfide units.

Experimental

Preparation of sulfide polymers:

Equimolar quantities of the monomers were placed in cyclohexane solution in a quartz test tube and irradiated with ultraviolet light for one to three days. The following polymers were prepared in this way and characterized by analysis.

Repeating Unit	Melting Point
$[(CH_2)_2\text{–}S\text{–}(CH_2)_6\text{–}S]$	82-86°
$[(CH_2)_4\text{–}S\text{–}(CH_2)_6\text{–}S]$	65-67
$[(CH_2)_5\text{–}S\text{–}(CH_2)_6\text{–}S]$	64-65
$[(CH_2)_6\text{–}S\text{–}(CH_2)_6\text{–}S]$	71-76
$[(CH_2)_{10}\text{–}S\text{–}(CH_2)_6\text{–}S]$	76-78
$[(CH_2)_{11}\text{–}S\text{–}(CH_2)_6\text{–}S]$	72-78
$[(CH_2)_{11}\text{–}S\text{–}(CH_2)_{10}\text{–}S]$	74-78
$[(p)\ (C_6H_4)\text{–}CH_2\text{–}(C_6H_4)\text{–}(CH_2)_2\text{–}S\text{–}(CH_2)_6\text{–}S\text{–}(CH_2)_2]$	84-88

Repeating Unit	Melting Point
[(p) (C_6H_4)-CH_2-(C_6H_4)-$(CH_2)_2$-S-$(CH_2)_2$]	105-108°
[$(CH_2)_2$-S-CH_2-$\underset{\displaystyle CH_3}{CH}$-$(CH_2)_6$-$\underset{\displaystyle CH_3}{CH}$-$CH_2$-S]	liquid
[$(CH_2)_2$-S-CH_2-$\underset{\displaystyle CH_3}{CH}$-$CH_6$-$CH_2$-S]	liquid

BIBLIOGRAPHY

1. Vaughan and Rust, J. Org. Chem., **7,** 473 (1942).
2. Coffman, U. S. 2,347,182, April 25, 1944, Chem. Abs., **39,** 226 (1945).
3. Braun and Plate, Ber., **67B,** 281 (1934).

VITA

The writer was born on May 23, 1923, in Lincoln, Nebraska. He attended the public schools there and graduated from Lincoln High School in 1940. He entered the University of Nebraska that fall and was granted the B. A. degree there in May, 1944. He entered the graduate school of the University of Illinois in June, 1944, and since then has held the following appointments:

Special Research Assistant in Chemistry (summer, 1944).

Allied Chemical and Dye Corporation Fellow (fall, 1944, to spring, 1945).

Special Research Assistant on the Rubber Research Program (summer, 1945).

Assistant in Chemistry (fall, 1945, to spring, 1946).

Monsanto Chemical Company Fellow in Chemistry (fall, 1946, to spring, 1947).

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549815_0011